

# SCIENCE FOR GLASS PRODUCTION

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## KINETICS OF CHROMIUM OXIDE TRANSFORMATIONS IN GLASS MELTING

Yu. A. Guloyan<sup>1</sup>Translated from *Steklo i Keramika*, No. 8, pp. 3–5, August, 2005.

The kinetics of chromium oxide transformations in glass batch under heating and in glass melt has been studied. The different degrees of transformation of  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  is demonstrated. The conditions of equilibrium between chromium oxides in the case of their simultaneous presence in glass melt is determined. The conditions of the interaction between chromium and iron oxides in the glass melt are investigated, including the surface layer in which an equilibrium between the colorant oxides can be achieved in accordance with the reaction conditions and the composition of the gaseous atmosphere. The low reaction velocities in the glass melt are due to its high viscosity and low values of diffusion coefficients.

The nature of the transformation of colorant compounds in glass melting is important for the technology of producing tinted glass, especially for automated glass container production. The processes of transformation of pigments occurring in the initial period of melting and later in the glass melt are insufficiently studied.

The study in [1] considered the conditions for the transformation and equilibrium of iron oxides. It is demonstrated that during melting of glasses containing iron oxides the transformations of the latter mainly occur in the solid phase and the ratio of two forms of iron oxides in glass melt is determined by the melt temperature. The valence state of iron oxides in industrial glass-melting furnaces does not satisfy the condition of equilibrium with the ambient medium due to a high melt viscosity and low values of the diffusion coefficients.

Chromium oxides are common colorants for container glasses; therefore, the present study is focused on the physicochemical parameters of transformations of chromium pigments.

We investigated the conditions of transformations of chromium oxides in melting industrial container glass. Chromium oxides were introduced in the amount of 0.10–0.25% (above 100%) of the main glass composition in the form of chromium anhydride  $\text{CrO}_3$ , potassium bichromate  $\text{K}_2\text{Cr}_2\text{O}_7$ , and chromium oxide  $\text{Cr}_2\text{O}_3$ . The content of chromium oxide in batches and glasses was found through chemical analysis

using the diphenylcarbide method. Laboratory electric furnaces adapted for the development and control of a corresponding atmosphere were used for experimental melting. The gaseous medium was characterized through partial oxygen pressure  $P_{\text{O}_2}$ . This parameter is universal and can be used to estimate both oxidizing and reducing conditions.

Compounds of hexavalent chromium introduced in the batch decompose under heating and produce  $\text{Cr}_2\text{O}_3$ . The nature of this transformation is determined by the thermal resistance of oxides which, in turn, is related to dissociation pressure.

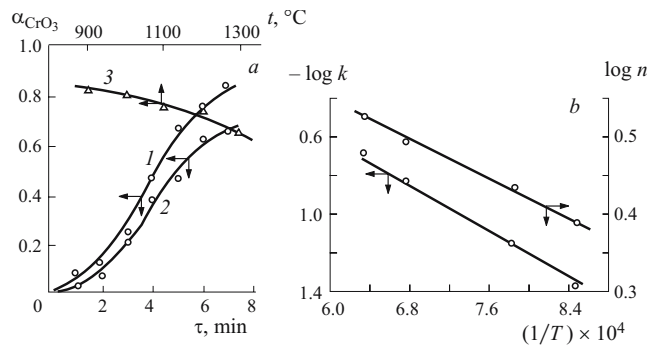
Figure 1a shows the transformation kinetics of the initial compounds in air ( $\log P_{\text{O}_2} = -1.68$ ) upon introducing  $\text{CrO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  into the batch. The parameter accepted as the main characteristic is the degree of transformation  $\alpha$ , i.e., share of the decomposed colorant. It can be seen that the rate of dissociation of  $\text{CrO}_3$  is higher than that of  $\text{K}_2\text{Cr}_2\text{O}_7$ . This is due to the fact that  $\text{K}_2\text{Cr}_2\text{O}_7$  under rapid heating does not decompose until the temperature of 800°C [2]. At the same time, the temperature has no perceptible effect on the degree of transformation of  $\text{CrO}_3$  when the batch is heated in air.

Processing experimental data using the kinetic equation from [3] shows that the transformation kinetics of  $\text{CrO}_3$  satisfies the equation

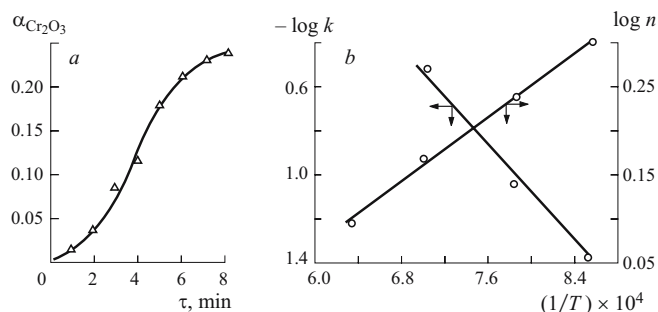
$$\alpha = 0.82 [1 - \exp(-k\tau^n)],$$

where  $\tau$  is the time;  $k$  and  $n$  are kinetic parameters.

<sup>1</sup> Research Institute of Glass, Gus'-Khrustalny, Vladimir Region, Russia.



**Fig. 1.** Kinetics of  $\text{CrO}_3$  transformation: *a*) variation in the degree of transformation  $\alpha$  for  $\text{CrO}_3$  depending on process duration at 900°C (1, 2) and temperature variation (3); *b*) dependence of kinetic parameters of  $\text{CrO}_3$  transformation on temperature; 1)  $\text{CrO}_3$ ; 2)  $\text{K}_2\text{Cr}_2\text{O}_7$ .



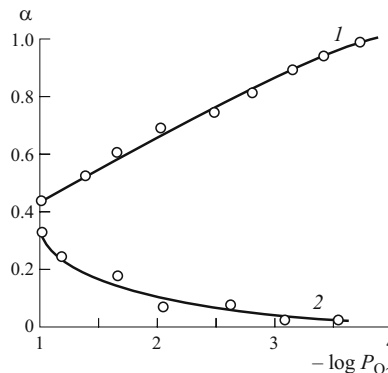
**Fig. 2.** Kinetics of  $\text{Cr}_2\text{O}_3$  oxidation in batch heating: *a*) variation in the degree of transformation  $\alpha$  for  $\text{Cr}_2\text{O}_3$  depending on process duration at 1000°C; *b*) dependence of kinetic parameters of  $\text{Cr}_2\text{O}_3$  oxidation on temperature.

The temperature dependence of the kinetic parameters suggests the existence of the surface and volumetric components in the process of  $\text{CrO}_3$  dissociation (Fig. 1*b*). The total activation energy of this process is made up of the activation energies of these components:

$$E = E_k + E_n = 67.3 \text{ kJ/mole.}$$

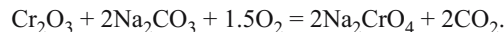
The process of  $\text{CrO}_3$  dissociation occurs mainly in the melt. On the one hand, chromium-oxygen links in the melt become significantly weaker and, as a consequence of intense thermal motion inside the melt, various ionic groups keep emerging and disintegrating, which facilitate the transport of oxygen to the surface and its subsequent desorption. On the other hand, the formation of  $\text{Na}_2\text{CO}_3$  melt creates favorable conditions for the oxidation of  $\text{Cr}_2\text{O}_3$ ; therefore, the process of  $\text{CrO}_3$  dissociation is delayed to a certain extent.

The process of  $\text{Cr}_2\text{O}_3$  oxidation in heating was investigated as well. Figure 2*a* shows the kinetics of  $\text{Cr}_2\text{O}_3$  transformation in batch heating in air without a reducing agent ( $\log P_{\text{O}_2} = -1.68$ ). It can be seen that the degree of transformation is insignificant, which is due to the high stability of



**Fig. 3.** Dependence of the degree of transformation  $\alpha$  for  $\text{CrO}_3$  (1) and  $\text{Cr}_2\text{O}_3$  (2) on partial pressure of oxygen.

$\text{Cr}_2\text{O}_3$  under the specified temperatures. A more complete oxidation requires a higher temperature and a longer exposure. The formation of  $\text{Na}_2\text{CO}_3$  melt facilitates the transport of oxygen and accelerates the oxidation of  $\text{Cr}_2\text{O}_3$  according to the following reaction:



Experimental data indicate that the process of  $\text{Cr}_2\text{O}_3$  oxidation as well has surface and volumetric components. The temperature dependence of kinetic parameters (Fig. 2*b*) and a certain activation energy of the process indicate the presence of adsorption phenomena on the surface of  $\text{Cr}_2\text{O}_3$  at the beginning of interaction:

$$E = E_k - E_n = 88 \text{ kJ/mole.}$$

The type of atmosphere influences the transformation of chromium compounds in batch heating. Figure 3 shows the dependence of the degree of transformation of chromium oxides on the partial oxygen pressure (exposure at 1000°C). It can be seen that  $\text{CrO}_3$  cannot be fully preserved under the conditions of the experiment even in an oxidizing atmosphere. Presumably the particular thermal resistance of  $\text{CrO}_3$  determined by dissociation pressure plays a significant role here. In this case the motive force of the process (the gradient between the partial pressure of oxygen in the furnace and the pressure of  $\text{CrO}_3$  dissociation) at the temperature of the experiment is quite substantial. It should be noted that at a temperature of 250°C the pressure of  $\text{CrO}_3$  dissociation already reaches the atmospheric pressure level. Therefore, at temperatures above 250°C the rate of  $\text{CrO}_3$  dissociation accelerates significantly. W. Weil and E. Thumen were able to achieve virtually complete preservation of  $\text{CrO}_3$  in melting chromium-bearing glass by applying oxygen pressure of 20 MPa [4]. In the case of  $\text{Cr}_2\text{O}_3$ , its oxidation proceeds with difficulty and intensifies in an oxygen atmosphere (Fig. 3).

To study the conditions of the transformation of chromium oxides in glass melt, sintered cakes and glasses obtained under a different redox potential were milled, melted,

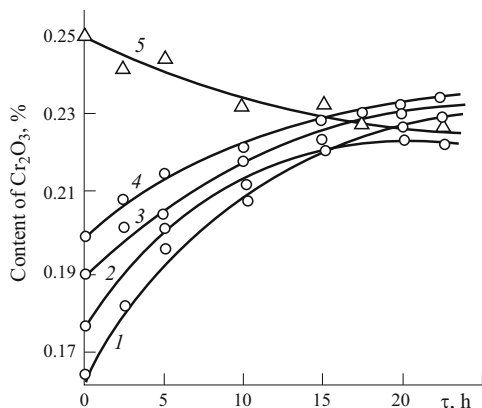


Fig. 4. Kinetics of variation in  $\text{Cr}_2\text{O}_3$  content. Sinters and glasses containing  $\text{CrO}_3$  (1–4) and  $\text{Cr}_2\text{O}_3$  (5).

and exposed at various temperatures in the form of a relatively thin layer (0.3–0.5 cm) in air. Depending on the redox potential of the melting atmosphere, the content of  $\text{CrO}_3$  in sinters and glasses varied from 0 to 40% of the total content of chromium oxides. The exposure temperature was 1200–1450°C, and the exposure duration was determined from the equilibrium between chromium oxides (found by chemical analysis).

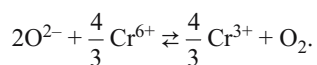
The dependence of  $\text{Cr}_2\text{O}_3$  content in glasses melts exposed in air at 1450°C shown in Fig. 4 characterizes the kinetics of reaching an equilibrium between the chromium oxides. It can be seen that this process takes long and is determined by oxygen diffusion. The residual quantity of  $\text{CrO}_3$  in glass is within the limits of 7–12% of the total chromium oxide content.

The determination of the diffusion coefficient yields results that are close to the data obtained in studying the transformation of iron oxides [1].

The equilibrium between the chromium oxides in glass is determined by the following reaction:



or, in ionic form



The equilibrium constant in this case is

$$K_e = (C_{\text{Cr}^{3+}}/C_{\text{Cr}^{6+}})^{4/3} P_{\text{O}_2}.$$

Equilibrium constants have been determined for the obtained experimental data based on the equilibrium content of chromium oxides. The temperature dependence of the equilibrium constant is shown in Fig. 5.

When tinting container glass with chromium oxides, one should take into account iron oxides penetrating into the glass from the source materials. Therefore it appears interest-

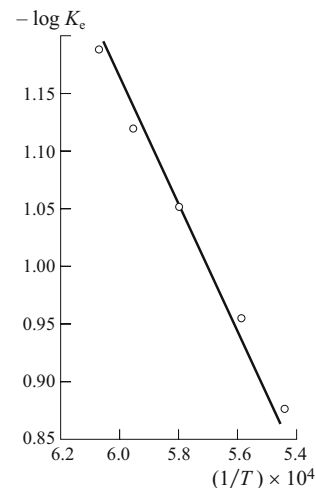


Fig. 5. Temperature dependence of equilibrium constant  $K_e$  of chromium oxides.

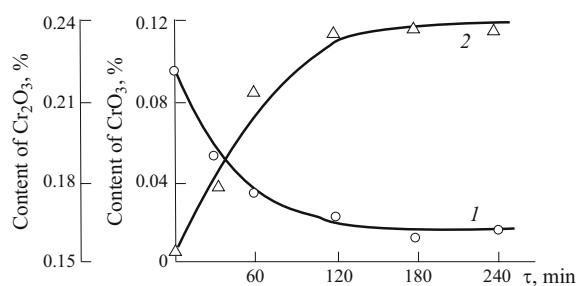
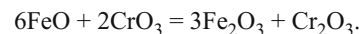


Fig. 6. Kinetic curves of variation in  $\text{CrO}_3$  (1) and  $\text{Cr}_2\text{O}_3$  (2) content in the surface layer.

ing to analyze certain factors of the interaction between iron and chromium oxides in glass melt. To study this interaction, well-melted glasses containing only chromium oxides (with an increased  $\text{CrO}_3$  content) and only iron oxides (with an increased  $\text{FeO}$  content) were mixed together and again melted at a temperature of 1480°C. The interaction kinetics was studied by consecutively taking out crucibles and performing a chemical analysis of glass to determine its content of chromium and iron oxides. It was found that the content of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in glass grows. This corroborates the data from the redox interaction between iron and chromium ions in the melt according to the following reaction:



Note the low velocity of the above reaction due to the high viscosity of the glass melt.

It has been noted that complete equilibrium between colorant oxides in large glass volumes can be achieved only after a long time and is impossible to reach in industrial glass-melting conditions. At the same time, the kinetics of interaction and the variation in the content of colorant oxides in the surface layers of glass are of interest. Considering this, an experiment was performed similar to the one described above. After exposure, a crucible with glass was annealed and glass samples with undisturbed surfaces were pre-

pared [5]. The content of the colorant oxides was found by means of chemical analysis.

The experimental results show that the content of oxides becomes stabilized within 2 – 3 h. In the presence of atmospheric oxygen ( $\log P_{\text{O}_2} = -1.68$ ) the latter of the specified reactions becomes reversible. Figure 6 shows the kinetics of the variation of chromium oxide content in the surface layer of thickness 0.05 cm. Considering the surface activity of chromium oxides [6], their content directly on the surface was enhanced due to adsorption.

Thus, the dependences characterizing the transformations of chromium oxides in batch heating and in glass melt have been identified. Chromium oxides, particularly  $\text{CrO}_3$  in melting industrial glasses, facilitate the oxidation of bivalent iron. The equilibrium content of colorant oxides in the surface layer of the melt can be reached in accordance with the reaction conditions and the composition of the gaseous atmo-

sphere. The low reaction velocities in the glass melt are determined by its high viscosity and low diffusion coefficients.

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